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Analysis of Furaneol in Tomato Using Dynamic Headspace Sampling with Sodium Sulfate

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High-flow dynamic headspace sampling with excess anhydrous sodium sulfate was found to be an effective method of isolating Furaneol from fresh tomatoes. Quantitative analysis was carried out by gas chromatography using maltol as internal standard. Furaneol was found in the highest concentrations (660−1100 ppb) in the summer crop of home-grown tomatoes and in some of the greenhouse hydroponically grown tomatoes, which are ripened on the plant before being transported to the supermarkets. Furaneol was found in the lowest concentrations (38−180 ppb) in the common ethylene-ripened, field-grown, supermarket tomatoes.

Keywords: *Tomato; Furaneol; concentration; dynamic headspace; analysis*

INTRODUCTION

Consumers have long been unhappy with the flavor of tomatoes commonly available at supermarkets, especially compared with ones that were grown in their own gardens.

Some of the authors have been carrying out studies over a number of years to identify the factors in tomatoes that are involved in the desirable fresh tomato flavor (*1*). Although the volatiles of tomatoes have been studied very thoroughly and >400 compounds listed as identified in tomato in a 1987 review (*2*), the presence of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Furaneol) in tomatoes had not been suspected until 1994 when 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone *β*-D-glucopyranoside was identified in tomatoes (*3*). This led to research that confirmed the presence of free Furaneol (*4*) in tomato in sufficient amounts to contribute to the flavor of the tomato.

Due to its high water solubility, analysis of Furaneol in most foods is time-consuming. It cannot be isolated (except in extremely low yields) by most of the commonly used methods for isolating volatile flavor compounds such as steam distillation [including steam distillation−extraction (SDE)] or conventional dynamic headspace sampling. It can be isolated by direct extraction of the filtered aqueous food with ether (*5*). For most foods, an extra step is necessary, such as the method of high-vacuum transfer (*6*) to separate Furaneol from nonvolatile material, before analysis by gas chromatography (GC). Some of the authors (*4*) had examined the use of a high-performance liquid chromatography (HPLC) method for the analysis but found it difficult to apply to the relatively low concentration of Furaneol in tomato. For the GC method, some of the authors had developed a relatively simple technique whereby water soluble volatiles can be isolated in reasonable yield, by mixing the food (and absorbing the moisture content) with excess anhydrous sodium sulfate and then carrying out dynamic headspace sampling in a closed loop system. One of the authors had applied this method to various corn products (*7*). The present study describes the application of this method to fresh tomatoes available from several different sources.

MATERIALS AND METHODS

Materials. Samples of tomatoes obtained from local supermarkets included (1) ordinary fresh market tomatoes, which are field-grown, picked when mature green, and ripened by the use of ethylene or products that produce ethylene; (2) tomatoes "on-the-vine", hydroponically grown in greenhouses in Arizona; (3) "hot house" tomatoes, grown hydroponically in greenhouses in California; (4) cherry tomatoes "on the vine"; and (5) "Roma" tomatoes, a high-solids processing-type tomato. (6) Samples of home-grown (El Cerrito, CA) tomatoes were also obtained, which were a cultivar known as Early Girl. Many different cultivars of fresh tomatoes are grown and sold, and the exact cultivars of the supermarket tomatoes that were purchased for this study are not known.

Diethyl ether (99+%, anhydrous, ACS reagent) was freshly distilled through a glass helix packed column, protected by the addition of 1−2 ppm of Ethyl Corp. antioxidant 330 and kept in the dark. Sodium sulfate (99.9%, certified ACS) was heated at 150° C for 3 h to remove any volatiles and stored in a tightly sealed glass jar with a metal lid.

Isolation of Furaneol from Tomato. The method was quite similar to that previously described for corn products (*7*). Tomatoes (30 g) were sliced and macerated in a Pyrex blending jar for 30 s at room temperature (21−25 °C). The blended tomatoes were held for 3 min (for enzyme action to occur), and then 100 g of anhydrous sodium sulfate added and blended thoroughly with the tomato. A sample (1.00 mL) of a standard solution of maltol (3-hydroxy-2-methyl-4-pyranone; 100 ppm) in water was then added, and the Na_2SO_4−tomato mixture was again blended and mixed thoroughly with a further 140 g of sodium sulfate. The mixture was then packed into a Pyrex glass column, 36 mm o.d. × 35 cm long, containing a coarse fritted disk at the lower end and ground spherical joints for connection to the closed loop dynamic headspace system. The lower end of the column was connected directly to a large (~10 g) Tenax trap. The outlet from the trap was connected via spherical joints and Teflon tubing to the recirculating Teflon diaphragm pump, the outlet of which was

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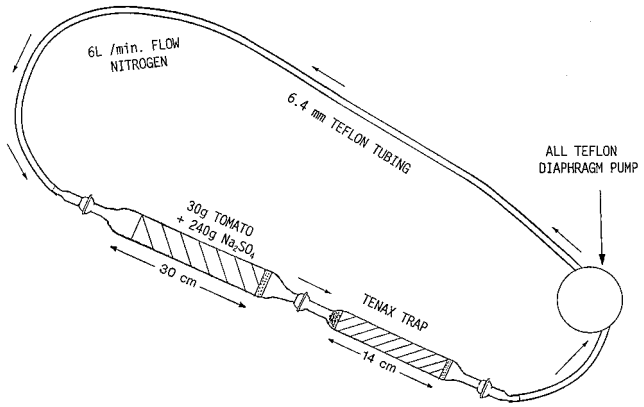

Figure 1. Diagram of the apparatus used for isolating the volatiles.

connected to the inlet of the Pyrex column, thus completing the loop (Figure 1). The complete system (placed behind a protective screen) was first flushed with nitrogen to displace the air before the loop was closed. The nitrogen was pumped around the loop at ~6 L/min and continued for 3 h. The trap was then removed and eluted with freshly distilled diethyl ether (50−100 mL). The ether extract was then concentrated to ~50 μL using a warm water bath and micro-Vigreux distillation column. Between analyses, cleaning was carried out by using an aspirator to draw ~2−3 L of boiling water through the Teflon pump (pump off) and tubing, followed by purified air for 2−4 h.

GC-MS Analysis. The capillary column was fused silica, 60 m long × 0.25 mm i.d., coated with DB-Wax (J&W Scientific, Folsom, CA). The column was held at 30° C for the first 4 min and then heated at 2 °C/min to 170 °C and held at this temperature for a further 30 min. The injector temperature was 170 °C with a 1/15 split. An HP5890 GC instrument was used, coupled to an HP 5971 quadrupole mass spectrometer.

Table 1. Concentration of Furaneol [2,5-Dimethyl-4-hydroxy-3(2*H*)-furanone] in Different Fresh Tomato Samples

type of fresh tomato	av concn, μg/kg	range found, μg/kg
home-grown (July)	880	660−1100
supermarket "hot house"	820	480−1100
supermarket "cherry on vine"	640	520−770
supermarket "on vine"	260	220−320
supermarket "Roma"	150	110−180
ordinary supermarket	110	38−180
green tomato	<8	all <8

Quantitative Analysis. The GC conditions used were similar to that described above except that the capillary column used had an i.d. of 0.32 mm. The internal standard was maltol (3-hydroxy-2-methyl-4-pyranone) at a concentration in water of 100.0 mg/kg (100 ppm). Flame ionization detection was used. Each isolation and analysis was carried out three or more times and the mean of the results obtained.

Recovery factors were obtained by carrying out experiments with known amounts of authentic Furaneol [for nine samples in the range equivalent to 160−2000 μg/kg (ppb)] added to 30 mL of water (containing 5% NaH_2PO_4 to give a pH of ~4.5, near that of tomato) and carrying out the isolation procedure as described above. Found data were plotted against amounts added.

RESULTS AND DISCUSSION

Figure 2 shows an example of a chromatogram of the volatiles isolated from a home-grown tomato sample using the DB-Wax capillary column. Table 1 lists the

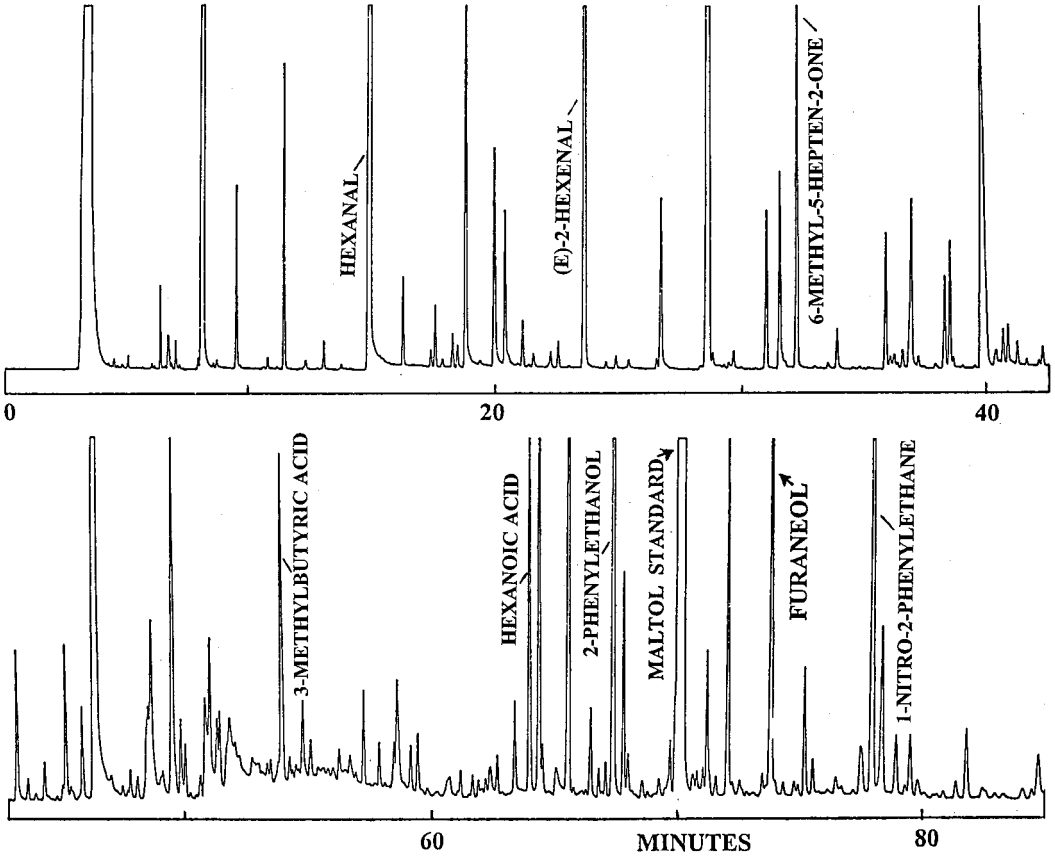

Figure 2. Capillary GC analysis (DB-Wax) of the volatiles isolated from home-grown tomatoes using the high-flow dynamic headspace sodium sulfate method. Peaks corresponding to Furaneol and maltol are indicated together with those of some other major components.

concentrations of Furaneol found in different types of tomatoes. Highest concentrations of Furaneol were found in the mid-summer (July) crop of home-grown tomatoes and in some hydroponically grown tomatoes, which are ripenened on the plant before being transported to the supermarket. The lowest concentration of Furaneol in ripe tomatoes was found in the standard lower priced supermarket tomatoes, which are usually field-grown, picked mature green, and ripened with ethylene (or ethylene-generating compounds). The odor threshold of Furaneol in water solution at pH 4.5 (close to the pH of tomatoes) had been found to be 31 μg/L (~31 ppb) of water (*4*). Except for the green tomatoes, all of the samples in Table 1 showed concentrations above this threshold value. The contribution of the "sweet" aroma character of Furaneol would, of course, be expected to be greater the higher its concentration in the tomato.

Preliminary studies had indicated that not all home-grown tomatoes showed high concentrations of Furaneol. Analyses of samples grown in the cooler months (September and October) showed considerably lower concentrations of Furaneol.

Isolation Method. Figure 1 shows a diagram of the apparatus used. The high-flow closed loop dynamic headspace method, using a Teflon diaphragm pump, had been described previously in a number of publications (*7*). A high-flow (6 L/min) of sweep gas is needed to transfer the Furaneol and maltol to the Tenax trap in a reasonable time. The much slower sweep rates of more conventional "purge and trap" systems are not effective for compounds of such low volatility.

Probably the most ideal internal standard to use is a stable isotope of the compound such as that described by Schieberle and Grosch (*8*). However, samples of such stable isotopes are not readily available. Maltol and ethylmaltol are chemically closely related to Furaneol but, unlike Furaneol, are very stable compounds. The authors have used ethylmaltol as an internal standard for some products that normally contain maltol, such as baked cereal products and processed tomato (e.g., paste). Fresh tomatoes, however, do not contain maltol, and so maltol was used in the present study.

Even though sodium sulfate was obtained from the same supplier, variations in particle size and adsorption efficiency were noticed. Occasionally it was necessary to use larger quantities (up to 100 g more) for adequate adsorption of the moisture.

Recovery of Furaneol in Model Systems. Recovery experiments with known amounts of Furaneol were carried out using a 5% water solution of NaH_2PO_4 to give a pH (4.5) approximating that of tomato. This showed a recovery that averaged 62 $\pm$ 6% (95% confidence, $n = 9$) relative to maltol for a Furaneol concentration range equivalent to 160−2000 μg/kg (ppb). Additional recovery studies using citric acid instead of NaH_2PO_4 gave similar values. This recovery factor was used in the calculation of the data for Table 1.

Variations of the Isolation Method. The closed loop, Grob type, system (*9*) is, in theory, the most efficient method for dynamic headspace sweeping, and this is consistent with the authors' experience in practice. However, a simpler, less costly, "open-ended" system, without the recirculating pump, can also be reasonably effective. Such an open-ended system could use a high flow of nitrogen from a cylinder as the sweep gas. With the method of isolating Furaneol by direct ether extraction (*5*), the Furaneol can be separated from higher boiling materials by using high-flow dynamic headspace sampling with a thin film of the extract (with ether evaporated) spread around the inside surface of a flask (*4*) or by using high-vacuum transfer (*6*).

Workable simplifications of this include using separatory funnel direct ether extraction (three times) of the blended tomato (saturated with NaCl) and using purified air as the sweep gas; the Furaneol showed no significant deterioration for the relatively short time (3 h) needed for the transfer.

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